

## Attachment C

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### 1. Introduction

5           In a process for producing semiconductors, there are many steps of forming insulating films such as silicon oxide film and silicon nitride film. A plasma CVD process (PECVD) is often used as the method for forming these insulating films. In such a process, it is necessary to clean a chamber inside depending on  
10 a frequency of film formation because solid sedimentation which is primarily film formation components is accumulated in the chamber and causes abnormal film formation and occurrence of particles. As the cleaning process, a dry cleaning has been widely pervaded in which the solid sedimentation is chemically  
15 changed to gaseous silicon tetrafluoride ( $\text{SiF}_4$ ) by active fluorine atoms to emit and remove. In order to generate the active fluorine atoms, the gas having the fluorine atom in a molecule is used, and generally the method is used in which plasma is generated from ethane hexafluoride ( $\text{C}_2\text{F}_6$ ) or nitrogen  
20 trifluoride ( $\text{NF}_3$ )<sup>1)</sup>. However, these gases are strong global warming gases, and the activity to restrict the use thereof has been activated after Third Conference of the Parties to the United Nations Framework Convention on Climate Change (COP3) held in Kyoto in 1997<sup>2)</sup>. In particular,  $\text{C}_2\text{F}_6$  is problematic  
25 because its emission matters in the cleaning process abundantly contain methane tetrafluoride ( $\text{CF}_4$ ) and undecomposed  $\text{C}_2\text{F}_6$  which have high global warming effects<sup>3)</sup>.

          As concrete measures for their reduction, the improvement of use efficiency by optimization of conditions and introduction  
30 of apparatuses for eliminating harmful effects have been already performed, and achieved great effects on emission reduction of global warming substances<sup>4,5)</sup>. In the future, it is required for the gas used in the cleaning process that a global warming potential (GWP) which the gas itself has is low and that the  
35 method for producing the gas is low environmental load. Cleaning

gases with low environmental load have been actively researched and developed worldwide<sup>6-8)</sup>. However, at present, there are few kinds of gases that satisfy many requirements as the cleaning gas, and more research and development are required.

5        We started from survey of physical properties of fluorine atom-containing compounds, focused on candidate gases, and actually performed optimization of the cleaning condition using a mass production model PECVD apparatus and its performance evaluation. As a result, we could find a potential of propene  
10 hexafluoride ( $C_3F_6$ ) as an alternative gas of  $C_2F_6$ . Here, we report new findings obtained for the cleaning mechanism by the gas in addition to the survey of the physical properties and the cleaning property.

## 15    2. Survey of physical properties

      It is necessary that the cleaning gas clear various conditions for practical application due to use in a large amount in addition to the cleaning performance and the environmental load. Specific requirements are (1) the cleaning  
20 performance being equivalent to or more than the performance of existing gases, (2) the environmental load being reduced by a total system, (3) having the physical property with low risk, (4) having vapor pressure capable of supplying in large amount such as concentrated supply, (5) being the gas abundantly  
25 present, capable of sufficiently assuring the amount supplied in the market, and (6) the total cost being equivalent to or less than the cost in the case using the existing gas. About 20 types of gases including substances having carbon atoms and fluorine atoms were surveyed to organize these requirements in terms of  
30 physical properties of the gas.

      Fig 1. shows indices of the cleaning performance. In the cleaning performance, it is an important point how the active fluorine atoms can be produced efficiently. Thus, a reaction in which intramolecular bonds were dissociated by receiving  
35 electron impact in plasma and an oxidization decomposition

reaction by co-existing oxygen were assumed as reaction paths for generating the fluorine atoms to compile each energy<sup>9)</sup>. It can be said that the gas present in a left lower area in the figure, which has low bond dissociation energy and exhibits a negative large value in reaction generating heat ( $\Delta H$ ) in the oxidation decomposition reaction generates the fluorine atoms most efficiently. In this area, fluorine gases are present, and the fluorine gas is cited as a candidate for a next generation cleaning gas. Efficacy of octafluoropropane ( $C_3F_8$ ) and octafluorocyclobutane ( $c-C_4F_8$ ) was confirmed by the bond dissociation energy, and the efficacy of  $C_3F_6$  and  $c-C_4F_8$  was confirmed by the oxidization decomposition reaction energy.

Subsequently, scales of environmental load property and risk were summarized in Fig. 2. The GWP of the gas was used for the environmental load property<sup>10,11)</sup>. For the scale of risk, placement numeric values for flammability, reactivity and toxicity of National Fire Protection Association were used, and a combined value of respective numeric values was shown<sup>12)</sup>.

The GWP depends on infrared absorption property and lifetime in air of the molecule. Meanwhile, the nature that the lifetime in air is short is a front-back relationship with becoming high reactivity and toxicity in the air. Therefore, in general, when the GWP is decreased, the scale of risk is increased, which is in inverse proportion tendency. However, only  $C_3F_6$  does not correspond to this tendency, and it has been demonstrated that the low GWP and the low risk are compatible in this gas.  $C_3F_6$  has a molecular structure having one double bond between two carbon atoms. It is known that this double bond is rapidly reacted with hydroxy (OH) radical in the air<sup>11)</sup>. Consequently, the lifetime of  $C_3F_6$  in the air becomes short and its GWP also becomes a very low value. However, it is extremely stable under an atmosphere in the absence of radical, and exhibits the physical property in which the low GWP and the low risk is alternately balanced. For  $C_3F_8$  and  $c-C_4F_8$  whose efficacy had been confirmed by the bond dissociation energy in the

cleaning performance shown in Fig. 1, the GWP was high although the scale of risk was very low.

In general,  $C_3F_6$  is widely pervaded as an intermediate raw material in fluorine resin industry, and is one of ideal gases in terms of stable supply to the market and production cost. In addition, it is the liquefied gas, but its vapor pressure is about 0.6 MPa which is relatively high at ambient temperature, and it is possible to sufficiently use for the cleaning process with high gas consumption amount.

From the results of the above survey,  $C_3F_6$  was employed, and its cleaning property using the mass production model PECVD apparatus was evaluated in comparison with  $C_2F_6$  which was the existing gas.

### 3. Evaluation of cleaning property

#### 3.1 Experimental methods

The mass production model PECVD apparatus (Precision 5000 supplied from AMAT) was used in evaluation of the cleaning property. In a procedure of the evaluation,  $SiO_2$  was formed into film, subsequently the cleaning was performed, and at that time, a trend of emitted components whose major component was  $SiF_4$  and a trend of luminescence intensity of the fluorine atoms in the chamber were measured. A schematic view of an experimental apparatus is shown in Fig. 3.

The emitted gas was analyzed by placing a Fourier transform infrared spectrophotometer (FTIR) behind a dry pump. FG120 supplied from Horiba and IGA2000 supplied from MIDAC were used as the FTIR. In an analytical condition, a light path length of a gas cell was 1 cm, and a decomposition capacity was  $2\text{ cm}^{-1}$ . A diaphragm pump was placed behind the gas cell, and about 2 slm of the gas with constant flow was introduced into the gas cell. In the emitted gas, many kinds of component gases coexist, and a dynamic range of their concentrations is also widely changed. Multicomponent analysis methods such as partial least squares (PLS) was used for quantitative analyses under

such a condition, and additionally analytical techniques for measured subjects and concentrations have been developed, and data were collected based on them<sup>13-16)</sup>. Concerning the gas emitted by the cleaning, it is necessary to evaluate a total amount of substances that contribute to the global warming and their influences as MMTCE. It was calculated from the measurement results by the FTIR and the GWP of the global warming substance.

### 10 3.2 Cleaning process

On the basis of the cleaning condition with  $C_2F_6$ , experiments were performed by changing a gas type, a flow, a mixed ratio with oxygen, pressure inside the chamber, a distance between electrodes and a cleaning time. Applied electric power with high frequency was 750 W that was constant.

In the cleaning process, two step cleaning where the cleaning with high pressure in which surrounding of the electrodes was effectively cleaned was first performed and then the cleaning with low pressure in which chamber walls and an emission system were cleaned was employed. A specific experimental procedure is shown below when  $C_2F_6$  is used.

<Experimental procedure>

Film formation (about 820 nm) → Cleaning → Seasoning

<Film formation condition>

25 Gas: tetraethoxysilane TEOS (700 mg/min) +  $O_2$  (310 sccm) + He (310 sccm)

Pressure: 10 Torr

Distance between electrodes: 5 mm

Rf power: 300 W

30 Film forming time: 60 s

<Cleaning condition>

- Cleaning with high pressure

Gas:  $C_2F_6$  (500 sccm) +  $O_2$  (600 sccm)

Pressure: 3.5 Torr

35 Distance between electrodes: 8 mm

Rf power: 750 w

Treating time: 45 s

-Cleaning with low pressure

Gas:  $C_2F_6$  (500 sccm) +  $O_2$  (600 sccm)

5 Pressure: 1.5 Torr

Distance between electrodes: 25 mm

Rf power: 750 w

Treating time: 25 s

<Seasoning condition>

10 Recipe: same as the film formation condition

Treating time: 10 s

### 3.3 Evaluation methods

The cleaning can be evaluated by the total amount of  $SiF_4$  emitted during the cleaning and the change of emitted concentrations with time. However, when the trace amount of cleaning residues remains, reliable determination can not be performed by the evaluation of one step. Therefore, it is usually necessary to perform a marathon test in which many wafers are processed and conduct multilateral evaluations. Thus, the post cleaning was performed by performing the standard cleaning, i.e., the cleaning with  $C_2F_6$  after performing the common cleaning to reliably evaluate a residual amount although one step is evaluated. The condition for the post cleaning was the same as in the  $C_2F_6$  cleaning, and the treating time was 20 s in each step. The condition was optimized by comparing both total amount of  $SiF_4$  and the trends in the common cleaning with those in the post cleaning. An example of the measurement is shown in Fig. 4.

## 30 4. Experimental results and discussion

### 4.1 Cleaning performance

#### 4.1.1 $C_2F_6$ cleaning

The change of  $SiF_4$  concentrations with time in the cleaning under the  $C_2F_6$  standard condition is shown in Fig. 5.

35 In the trend of  $SiF_4$  emission, much emission was observed

in an early stage of the cleaning. When the cleaning with high pressure is changed to the cleaning with low pressure, there are few seconds of plasma off time required for regulating the distance of electrodes and the pressure. The emission of  $\text{SiF}_4$  was once stopped in the meantime, and subsequently the emission was started again when the cleaning with low pressure was performed. In the post cleaning, the  $\text{SiF}_4$  emission was slightly observed, and this appeared to be derived from the material such as quartz glass in the chamber. Thus, this level was set as a background.

#### 4.1.2 $\text{C}_3\text{F}_6$ cleaning

The  $\text{C}_3\text{F}_6$  cleaning was performed under the condition of the same treating time as in the  $\text{C}_2\text{F}_6$  standard cleaning. The relationship of the  $\text{SiF}_4$  emission concentration with the treating time in the  $\text{C}_3\text{F}_6$  cleaning is shown in Fig. 6 compared with that in the  $\text{C}_2\text{F}_6$  cleaning.

In the  $\text{C}_3\text{F}_6$  cleaning, the concentration of  $\text{SiF}_4$  emitted in the early stage of the cleaning was lower than that in the  $\text{C}_2\text{F}_6$  cleaning. The trend of the  $\text{SiF}_4$  emission was stable, and the emission converged and reached an end point at the completion of the cleaning time. Total amount of  $\text{SiF}_4$  emitted during the cleaning was the same as in the  $\text{C}_2\text{F}_6$  cleaning. In the post cleaning under the condition 3, both the total amount of emitted  $\text{SiF}_4$  and the trend favorably corresponded to those in the  $\text{C}_2\text{F}_6$  cleaning. However, under the condition 2, the level of emitted  $\text{SiF}_4$  was higher than the background, and the cleaning residues were observed.

For the conditions of the cleaning with  $\text{C}_3\text{F}_6$ , condition dependency for various factors such as mixing ratio of  $\text{C}_3\text{F}_6$  and  $\text{O}_2$ , pressure of chamber inside at the cleaning with high pressure and total gas flow was compiled using the total amount of emitted  $\text{SiF}_4$  in the post cleaning as an indicator. The results are shown in Figs 7 to 9.

For the mixing ratio of  $\text{C}_3\text{F}_6$  and  $\text{O}_2$ , a minimum value was

observed at a  $C_3F_6$  concentration of about 20%. It was found that a higher oxygen concentration became a preferable condition in the  $C_3F_6$  cleaning than in the  $C_2F_6$  cleaning because the  $C_2F_6$  concentration of about 50% was the optimal condition in the  $C_2F_6$  cleaning.

The pressure of chamber inside in the cleaning with high pressure was minimum around 5 to 6 Torr. The optimal condition in the  $C_2F_6$  cleaning was around 4 Torr, and it was found that the preferable condition in the  $C_3F_6$  cleaning was in the relatively higher pressure side.

Total gas flow dependency was minimum at about 600 sccm. It was found that the number of total fluorine atoms which entered into the chamber could be increased by increasing the flow but the cleaning effect was reduced by contrast.

In order to compare the optimal conditions of  $C_2F_6$  and  $C_3F_6$ , a residence time of the gas in the chamber in the cleaning with high pressure was calculated. A calculating formula is shown in the formula (1).

$$\tau = P_r V_r T_s / P_s Q T_r \quad (1)$$

$P_r$ : Pressure of chamber inside (Torr)  
 $P_s$ : Standard pressure (760 Torr)  
 $V_r$ : Volume of chamber inside (4700 cm<sup>3</sup>)  
 $Q$ : Total gas flow (sccm)  
 $T_r$ : Temperature of chamber inside (333 K)  
 $T_s$ : Standard temperature [ 273 K)

As a result of the calculation, the residence time of  $C_3F_6$  in the  $C_3F_6$  cleaning was about 3.5 folds compared with the  $C_2F_6$  cleaning. The residence time will be described in more detail in a section of cleaning mechanism.

#### 4.2 Environmental property

The environmental load due to the cleaning is evaluated by the analysis of components emitted by the cleaning steps. In the present experiment, chemical components that contribute to the global warming were quantitatively analyzed by FTIR. Analysis



results for  $C_2F_6$  and  $C_3F_6$  are shown in Figs. 10 and 11.

In the  $C_2F_6$  cleaning, it was found that decomposition efficiency of the gas was about 30% which was low and a reaction by-product  $CF_4$  was abundantly generated. Meanwhile, in the  $C_3F_6$  cleaning, the decomposition efficiency of the gas was 99% or more, and the generation of  $CF_4$  was also widely reduced. MMTCE was calculated from the formula (2).

$$MMTCE = \sum(Q_i \times 12/44 \times GWP_{100i})/10^9 \quad (2)$$

$Q_i$ : emission weight of component  $i$  (kg)

As a result of the calculation, the MMTCE of  $C_2F_6$  and  $C_3F_6$  were  $8.5 \times 10^9$  and  $3.0 \times 10^{10}$ , respectively, and the MMTCE in the  $C_3F_6$  cleaning was dramatically low.

#### 5. Cleaning mechanism

In the cleaning with  $C_3F_6$ , the same amount of  $SiF_4$  was emitted in the same treating time as in the  $C_2F_6$  cleaning. The MMTCE in the  $C_3F_6$  cleaning was reduced by 95% or more compared with the  $C_2F_6$  cleaning, and thus, the environmental property is widely enhanced. When the  $C_3F_6$  cleaning was compared with the  $C_2F_6$  cleaning, there were large differences in three issues, i.e., the residence time of the gas in the chamber, the decomposition rate of the gas during the cleaning and the generation trend of  $CF_4$ . Here we will discuss what mechanisms give these performances.

First, the decomposition rate of the gas will be discussed. The decomposition rates of the gas were about 30% and 99% or more in the  $C_2F_6$  cleaning and the  $C_3F_6$  cleaning, respectively. First, as the mechanism for the gas decomposition, the bond dissociation reaction by electron impact in plasma is speculated. Bond dissociation energy is 4.3 eV in C-C bond and 5.5 eV in C-F bond in the case of  $C_2F_6$ , and 4.6 eV in C=C bond and 4.8 eV in C-C bond in the case of  $C_3F_6$ . Therefore, no large difference is observed between  $C_2F_6$  and  $C_3F_6$  in bond dissociation energy between carbon atoms, whose contribution to the decomposition rate appears to be low.

Subsequently, the contribution of the chemical reaction was investigated. It is known that  $C_3F_6$  has a double bond between two carbon atoms and generally various radicals are rapidly added to the bond<sup>17)</sup>. The gas introduced into the chamber during the cleaning is formed into plasma, and at that time, various radicals such as fluorine atoms, oxygen radicals and oxygen atoms are generated. Thus, in gas phase chemical reactions in the  $C_3F_6$  cleaning, it is speculated that these radicals are actively reacted with  $C_3F_6$  molecules. On the contrary, in the case of saturated fluorocarbon molecules such as  $C_2F_6$ , the gas is not decomposed in the presence of radicals because  $C_2F_6$  has no active bond in the molecule. Therefore, it is presumed that the radical addition reaction is greatly contributed in the gas phase chemical reactions in the  $C_3F_6$  cleaning and consequently the gas decomposition rate was exponentially enhanced.

Subsequently, the mechanism for  $CF_4$  generation will be discussed. The mechanism for  $CF_4$  generation is a recombination reaction of  $CF_x$  radicals with fluorine atoms. In the case of the  $C_2F_6$  cleaning, when the emission amount of  $SiF_4$  was reduced, the generation amount of  $CF_4$  was increased. This tendency indicates that the recombination reaction of  $CF_x$  radicals with fluorine atoms progresses predominantly in the pure gas phase chemical reaction process where the solid silicon oxide subjected to the cleaning is not present. Meanwhile, in the case of the  $C_3F_6$  cleaning, the generation rate of an oxygen-containing compound was high, and even when the emission of  $SiF_4$  was prone to decrease, the change of  $CF_4$  generation amount was low. This result indicates that the plasma gas phase reaction is stable from beginning to end. In the  $C_3F_6$  cleaning, the generation rate of carbonyl difluoride ( $COF_2$ ) which is incomplete oxide is high, and it is speculated that there is a disappearance process of the fluorine atoms which become active species. In the present experiments, it was demonstrated that the more efficient cleaning could be performed under the condition in which the residence time of the gas in the chamber was prolonged. This is

considered because a generation reaction path of  $\text{COF}_2$  is inhibited or generated  $\text{COF}_2$  is further decomposed. Therefore, in the  $\text{C}_3\text{F}_6$  cleaning, it is thought that the more efficient cleaning can be performed by prolonging the residence time of the gas and  
5 further increasing plasma discharge power.

## 6. Summary

Physical properties of various fluorine based gases were surveyed as the alternative gas of the  $\text{C}_2\text{F}_6$  cleaning gas in the  
10 PECVD chamber cleaning. As a result, the efficacy of  $\text{C}_3\text{F}_6$  could be found. In addition, by using the mass production model PECVD apparatus, the condition for the cleaning with  $\text{C}_3\text{F}_6$  was optimized, and the cleaning performances of  $\text{C}_3\text{F}_6$  were compared with those of  $\text{C}_2\text{F}_6$ . Consequently, it was demonstrated that the cleaning  
15 performances were equivalent and the MMTCE could be reduced by 95% or more.